

UNIVERSITY OF TORONTO
STUDIES

PAPERS FROM THE CHEMICAL
LABORATORIES

No. 86: THE THEORY OF THE D
DETERMINING TRANSPORT NUMBE

(REPRINTED FROM ZEITSCHRIFT FÜR PHYSIKALISCHE C

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CHEMICAL

THE DIRECT METHOD OF
NUMBERS, BY W. LASH MILLER

PHYSIKALISCHE CHEMIE, Bd. L., VIII)

Y: PUBLISHED BY

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**The theory of the direct method of d
transport numbers.**

By

W. Lash Miller.

(With 2 figures in text.)

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The theory of the direct method of determining transport numbers.

The 'transport number of any component of an electrolytic solution, as defined by Hittorf, gives the number of electrochemical equivalents of that constituent transported from one electrode compartment to another during the passage of 96 540 coulombs through the solution. It may be determined either by quantitative analysis of the contents of the electrode compartments before and after the passage of a measured amount of electricity (Hittorf's or analytical method), by observation of the motion of the boundary separating two solutions (meniscus or direct method), or by thermodynamic inference from E. M. F. determinations etc. (thermodynamic method).

The theory of the 'direct' method has been developed by Kohlrausch¹), Weber²), Masson³), Abegg⁴) and others, i. e. among the experimental workers in this field the impression seems to have grown up that 'directly' determined transport numbers need not necessarily agree with those obtained by the analytical method⁵). The following argument, which differs from those of Kohlrausch and others in avoiding all references to rates, mobilities, current, and other functions involving time, and which makes no assumption as to the constitution (whether complex or not) of the ions of the solutions involved, shows that transport numbers properly calculated from observations of the motion of the meniscus must be identically the same as those obtained

¹) Wied. Ann. 62, 237 (1897).

²) Ber. d. d. chem. Ges. 936 (1897).

³) Zeitschr. f. physik. Chemie 29, 501 (1899).

⁴) Zeitschr. f. physik. Chemie 40, 737 (1902).

⁵) For instance, Zeitschr. f. physik. Chemie 44, 575 (1903); Phil. Trans. 205 A, 99 (1905).

by the analytical method; in fact, that the 'meniscus method' is but a modification of the method of Hittorf, in which the amounts of the various constituents of the solution transported are determined by volume measurements instead of by quantitative chemical analysis.

Two salts with common ion.

Figure 1 represents the longitudinal section of a cylindrical tube of radius r , through which the (positive) electric current flows in the direction indicated by the arrow. At the beginning of the experiment the tube is filled with solutions of AS and AZ , meeting at ab ; and it is assumed that the boundary between these solutions (hereafter termed the "meniscus") although moving along the tube, remains sharp

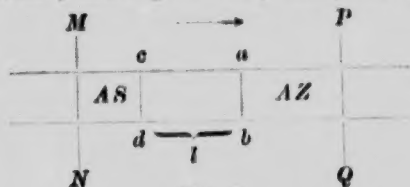


Fig. 1.

and distinct throughout the experiment. Under the influence of the current the constituent A of the solutions moves in the direction of the positive current of electricity, S and Z move in the opposite direction; so that, in Faraday's sense although not necessarily in the sense of the modern theory of solutions, A , S and Z are the 'ions' present.

Let cd , at a distance l cm. from ab , represent the position of the meniscus after the passage of 96540 coulombs; $\pi l r^2$ cc of the AS solution have therefore been replaced by a solution of AZ . The remaining solution of AS , to the left of cd , retains its original composition¹⁾, and consequently $\pi l r^2 \Sigma$ grams of the component S (Σ representing the number of grams of S in one cc of the AS solution) must have passed the stationary section MN . This number, $\pi l r^2 \Sigma$, may be termed the "uncorrected gram transport number" of the ion S ; and if the concentration be expressed in gram equivalents of S per cc, σ , then $\pi l r^2 \sigma$ gives its "uncorrected equivalent transport number". Hittorf's transport number is defined as the number of equivalents of S which during the

¹⁾ The concentrations and the electrical conditions are the same at any two sections through the homogeneous solution, consequently the amounts transported through the two sections must be the same, and there can be no accumulation or change of concentration between them.

passage of 96540 coulombs cross a boundary stationary with respect to the water of the solution, not, like MN , stationary with respect to the walls of the tube; hence the use of the word "uncorrected". Neglecting the correction, and writing n_s for Hittorf's transport number, and N_s for the gram transport number,

$$\pi l r^2 \Sigma = N_s, \quad \pi l r^2 \sigma = n_s. \quad (1)$$

This is the fundamental expression connecting the transport number with the motion of the meniscus; it shows (1) that, subject to a correction for the expansion and contraction caused by electrolysis, the transport number as defined by Hittorf may be deduced from observations of the motion of the meniscus, no matter whether the ions of the solution be 'complex' or 'simple'; and (2) that in carrying out the experiments, the quantities to be determined are: the concentration of the solution, the cross-sectional area of the tube, and the distance moved per coulomb by the meniscus.

The concentration (Z' , ζ') of the new solution of AZ formed to the right of cd by the electrolysis, is not necessarily the same as that of the solution with which the tube was originally filled (Z , ζ); nor does the meniscus separating these two AZ solutions necessarily remain fixed at ab . If however it be supposed that the tube was originally filled with a solution of AZ of the concentration Z' , it is obvious that

$$\pi l r^2 Z' = N_z', \quad \pi l r^2 \zeta' = n_z \quad (2)$$

because the lefthand member gives the number of grams (or equivalents) of Z which during the passage of 96540 coulombs have crossed the stationary section PQ ; and as the motion of the meniscus AS/AZ is independent of the existence of a meniscus $AZ_{conc.}/AZ_{dil.}$, it is allowable to apply Equ. (2) in the general case, where the concentration of the new solution (Z') differs from that of the original (Z). Methods of determining the transport number based on Equ. (2) are more difficult of execution than those based on Equ. (1), because they involve an experimental determination of ζ' , while σ is known.

From (1) and (2) there follows

$$\frac{N_s}{N_z} = \frac{\Sigma}{Z'}, \quad \frac{n_s}{n_z} = \frac{\sigma}{\zeta'} \quad (3)^1$$

a relation, like (1) and (2), wholly independent of special assumptions.

¹) Kohlrausch, loc. cit. p. 238; Masson, loc. cit. p. 515.

Two solutions of different concentrations.

If in place of solutions of two salts, AS and AZ , the cylinder be supposed filled with two solutions of the same salt AZ but of different concentrations viz: Z and Z' grams (or ζ and ζ' equivalents) of the constituent Z per cc respectively, the same method of argument may be employed. To fix the ideas, let Z be greater than Z' ; if then the transport number of the anion Z increase with the concentration of the solution, the meniscus will move against the current in fig. 2, and vice versa. After the passage of 96540 coulombs, n_z equivalents

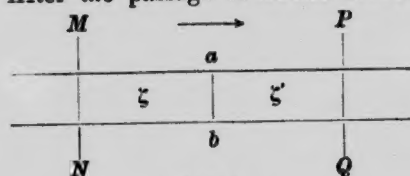


Fig. 2.

of Z have passed MN , and only n'_z have passed PQ ; so that if it be assumed that the solutions on either side of the meniscus retain their initial concentrations,

$$n_z - n'_z = \pi l r^2 (\zeta - \zeta')$$

$$\text{whence } l = \frac{1}{\pi r^2} \frac{n_z - n'_z}{\zeta - \zeta'}. \quad (4)$$

Absence of motion would consequently indicate that the transport number was independent of the concentration of the solution¹⁾.

In any attempt to realize the conditions of the argument in practice, the boundary between the two solutions of different concentrations would consist of a more or less broad diffusion band; this may be considered as consisting of a number of parallel "menisci" between pairs of solutions whose concentrations increase from ζ to ζ' in fig. 2. Assuming that n_z increases with increase in the concentration, all of these will move against the current; and if n_z be a linear function of the concentration, i. e., if $\frac{dn_z}{d\zeta} = \frac{n_z - n'_z}{\zeta - \zeta'} = \text{const.}$, all will move the same distance, and the breadth of the diffusion band will not be affected by the migration. If however $\frac{n_z - n'_z}{\zeta - \zeta'}$ decrease with increase in ζ , i. e. if $\frac{d^2 n_z}{d\zeta^2}$ be negative, the menisci to the right in fig. 2 will overtake those to the left, thus sharpening the boundary, and vice versa²⁾.

¹⁾ Kohlrausch, loc. cit. p. 235.

²⁾ Kohlrausch, loc. cit. p. 236.

Conditions of maintenance of meniscus.

Thus the method of the present paper enables one, in a simple case, to predict the effect of current on the stability of the meniscus itself. To solve the problem in general however, it is necessary to discuss the result of electrolysing a solution whose concentration (as regards one ion at least) varies along the path of the current; under these conditions the assumption made on page 437 (that the composition of the solution at any point is unaffected by the passage of the current) can no longer be made, and the simple method of treatment employed in this paper is inapplicable. Whetham's principle¹⁾ — that to ensure a sharp meniscus the specifically slower ion must follow the specifically faster — is of great practical utility, and Kohlrausch has deduced a number of generalizations applicable to solutions in which the mobilities of the ions involved do not vary with their concentrations (total dissociation)²⁾; but the general solution can be attained only through the application of Arrhenius' theory of electrolytic dissociation, and in particular his theory of isohydric solutions³⁾, to establish the necessary connection between the concentrations and the (empirical) mobilities of the components of a solution containing several salts.

Arrhenius has shown, for instance, that in an aqueous solution containing acetic acid and sodium acetate in approximately equal quantities, the dissociation of the acetic acid and consequently the participation of the hydrogen ion in the transport of an electric current is very slight; it follows from this, that a stable meniscus may be expected between acetic acid and sodium acetate solutions if the (positive) current flows from the former to the latter, *i.e.* if the hydrogen ion follows the sodium ion. Experiments by Mr. Dawson and Mr. Graham in this laboratory confirm this conclusion, and, it is hoped, may lead to a satisfactory determination of the transport number of acetic and other weak acids by the direct method.

Summary.

1. The theory of the "direct" method of determining transport numbers may be dealt with without introducing rates, mobilities, current, or other functions involving time, and without making any assumptions as to the constitution of the electrolytes.

¹⁾ Theory of Solution, p. 220 (1902).

²⁾ Wied. Ann. 62, 219.

³⁾ Wied. Ann. 30, 51 (1887); Zeitschr. f. phys. Chemie 5, 1 (1890).

2. Transport numbers properly calculated from observations of the motion of the meniscus must be identically the same as those obtained by the analytical method; for the meniscus method is but a modification of the method of Hittorf in which the amounts of the various constituents of the solution transported are determined by volume measurements instead of by quantitative chemical analysis.

3. The problem of the stability of the boundary between two electrolytes can not be solved in general without special assumptions as to the constitution of the electrolytes, such as are afforded by Arrhenius' theory of electrolytic dissociation and his theory of isohydric solutions.

The University of Toronto, September 1908.



